THE GENERATOR COORDINATE APPROXIMATION FOR MOLECULES: A REVIEW

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Abstract

The generator coordinate approximation is a non-adiabatic theory of molecular systems. Its fundamental outlines were developed during the 1970's. Further analysis and first applications were published during the 1980's. In this paper, we review the present status of the theory.

1. Introduction

The Born-Oppenheimer approximation [1] or separation of electronic and nuclear motion is without any doubt the cornerstone of theoretical (or mathematical) chemistry and has generated the primary concepts (electronic states, potential energy surfaces, equilibrium configurations, dipole moment functions, ...) in terms of which we talk about molecular properties.

The Born-Huang expansion [2] of the total molecular wave function in the complete set of electronic states yields a set of coupled differential equations that constitute an exact representation of the full molecular Schrödinger equation. Neglecting the coupling between different electronic states, a good approximation in the absence of (near) electronic degeneracies, leads to the so-called adiabatic approximation. The associated wave function is then a product of an electronic state and a nuclear wave function. All discrepancies (with the exact solution) caused by this approximation go under the name of "non-adiabatic effects" and are due to the fact that the nuclear kinetic energy operator is not diagonal in the electronic basis. The standard computational strategy to go beyond the adiabatic approximation is to include in the coupled equations those electronic states for which the off-diagonal matrix elements of the nuclear kinetic energy are significant. Thus improving upon the adiabatic approximation amounts to replacing a single product by a sum of products. This procedure is not satisfactory from the theoretical point of view since there is no way of estimating the convergence of the results. From a practical point of view, it turns out to be
cumbersome to calculate several electronic states to the same accuracy, i.e. it is difficult to get a balanced input for the method.

The alternative is to try to extract from a single electronic state more information than is accomplished by the adiabatic approximation. It is in this spirit that the generator coordinate approximation (GCA) was devised by replacing the product state by a convolution product. The resulting trial state in which electronic and nuclear motions are explicitly correlated (by the non-product form) can be variationally optimized and leads to the reformulation of the theory of molecules in terms of new concepts (nuclear weight function, energy integral kernels, dipole integral kernels, ... ) alternative to the traditional ones (nuclear wave function, potential energy surfaces, dipole function, ... ).

A summary of GCA theory and applications up to 1980 was given in a previous review [3]. The state of affairs at that time was the following: the formulation of the GCA theory, especially for diatomic molecules, was developed in sufficient detail to show the relevant new concepts involved, to pinpoint the computational implications. An exactly soluble test problem had shown that the GCA is capable of removing the non-adiabatic error of order $\kappa^6$. A number of open problems could be formulated, the most immediate of which were the following:

1. In order to establish generally whether the GCA energetically improves the adiabatic approximation, one should carry out a full perturbation scheme (in the spirit of Born–Oppenheimer perturbation theory) of the GCA nuclear equation, i.e. the Wheeler integral equation.

2. To confirm the analytical results of such an analysis, a fully numerical application of the GCA to a realistic molecular system was called for.

3. The Dunham series [4], the term value formula that is so successful in parametrizing diatomic spectra, should have its counterpart in the GCA. The problem remained to establish the relation between the Dunham coefficients and the basic theoretical concepts of the GCA.

4. Although the principle involved in the GCA ansatz seemed acceptable for the energy region near a potential minimum, there was no such immediate intuitive support for the relevance of the GCA near electronic degeneracies. A test of the GCA in such cases of strong non-adiabatic effects was necessary.

Each of the open problems mentioned above has been addressed during the past decade. The present state of affairs, of which this paper gives an overview, is as follows:

1. A perturbation analysis of the GCA allows one to clearly distinguish between non-adiabatic contributions, of various orders in $\kappa$, to the GCA energy. Of particular importance is the propagation of inaccuracies in the input electronic state to the final GCA results.

Throughout this paper, $\kappa$ denotes the Born–Oppenheimer perturbation parameter, i.e. $(m/M)^{1/4}$, where $m$ is the electron mass and $M$ the average nuclear mass of the molecule.